Standard Approaches for Statistical Assessment of Data

QA Peer Review Meeting

April 29, 1999

Chicago, IL

General Statistical Approaches

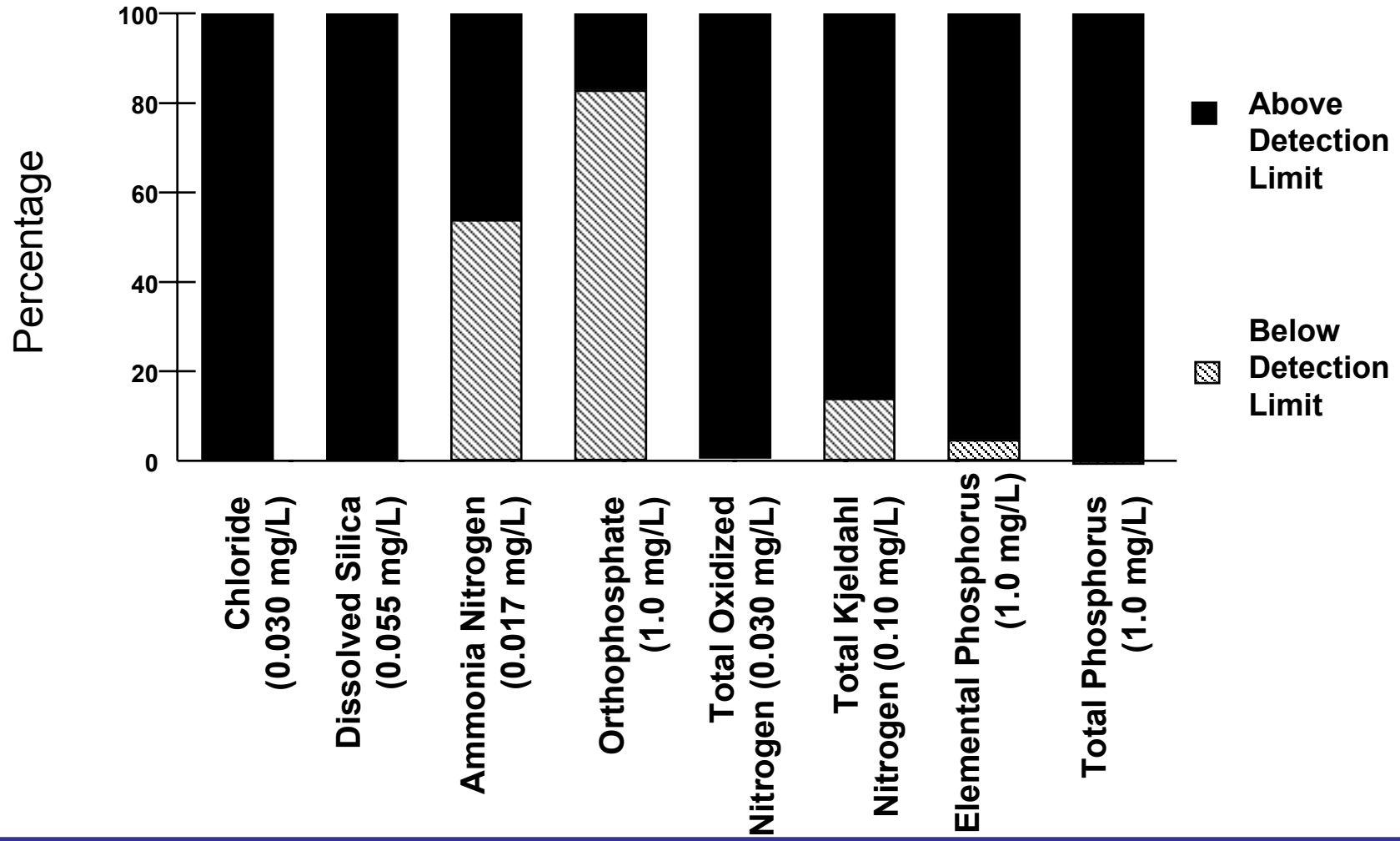
- **Sensitivity**
  - System (SDLs- estimated through analysis of field blanks)
  - Analytical (MDL, IDL, DDL, UDL)
- **Precision**
  - System - field duplicates
  - Analytical - laboratory duplicates
- **Bias**
  - System - Recoveries of spiked field samples (FCM)
  - Analytical - Recovery of spiked laboratory samples, reference materials, or other QC samples (SCF, LPC, SRM)
- **Percentage of Total Variability due to Sampling and Analytical Measurement Uncertainty**

Sensitivity

- Assessed through detection limits
  - System Detection Limit (SDL)
  - Method Detection Limit (MDL)
  - Daily Detection Limit (DDL)
  - Sample Specific Detection Limit (UDL)
- Compare limits to RFS samples (% below)
- For DDL and UDL, examine distribution and trends in limits

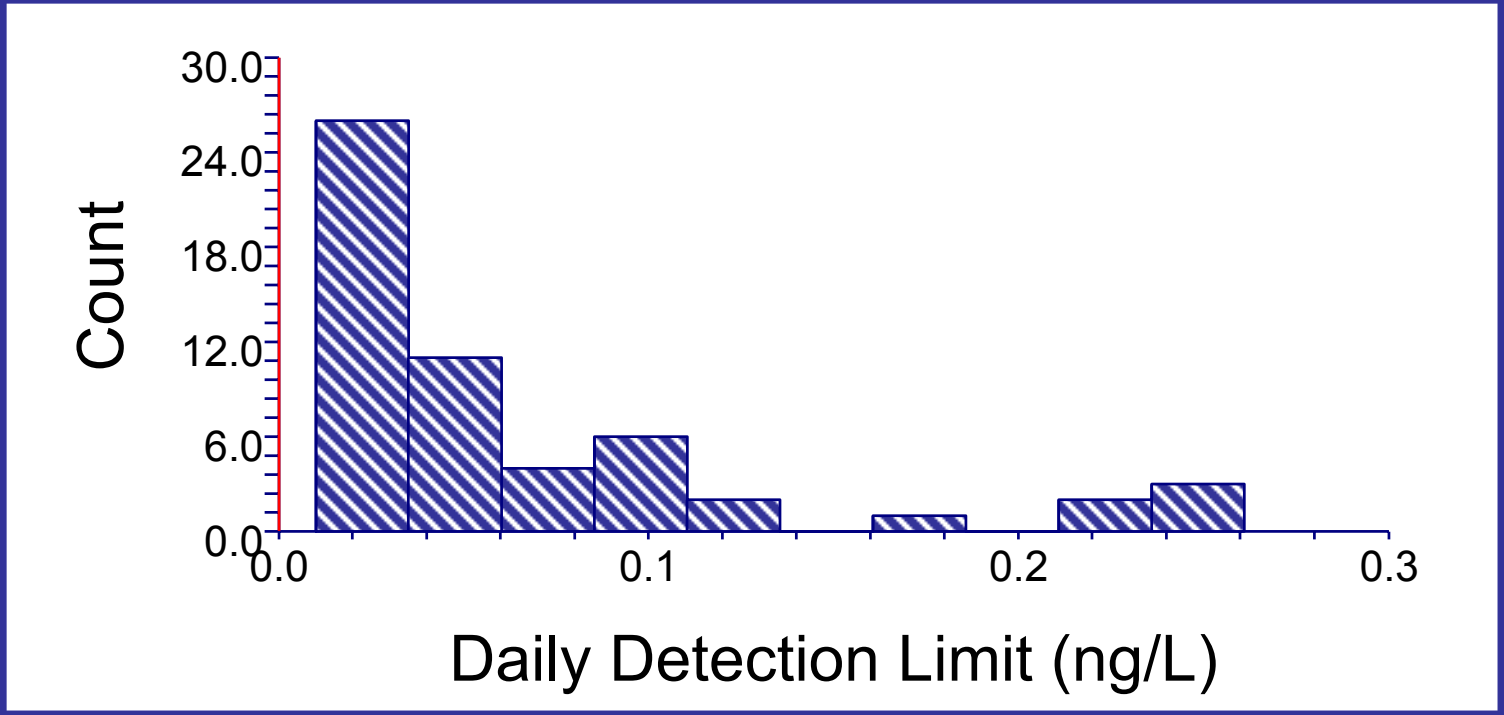
Sensitivity

Percentage of RFS Sample Results Relative to Detection Limit - GRLN



Sensitivity

Frequency of Daily Detection Limits - MDLH



- 55 limits calculated

Sensitivity

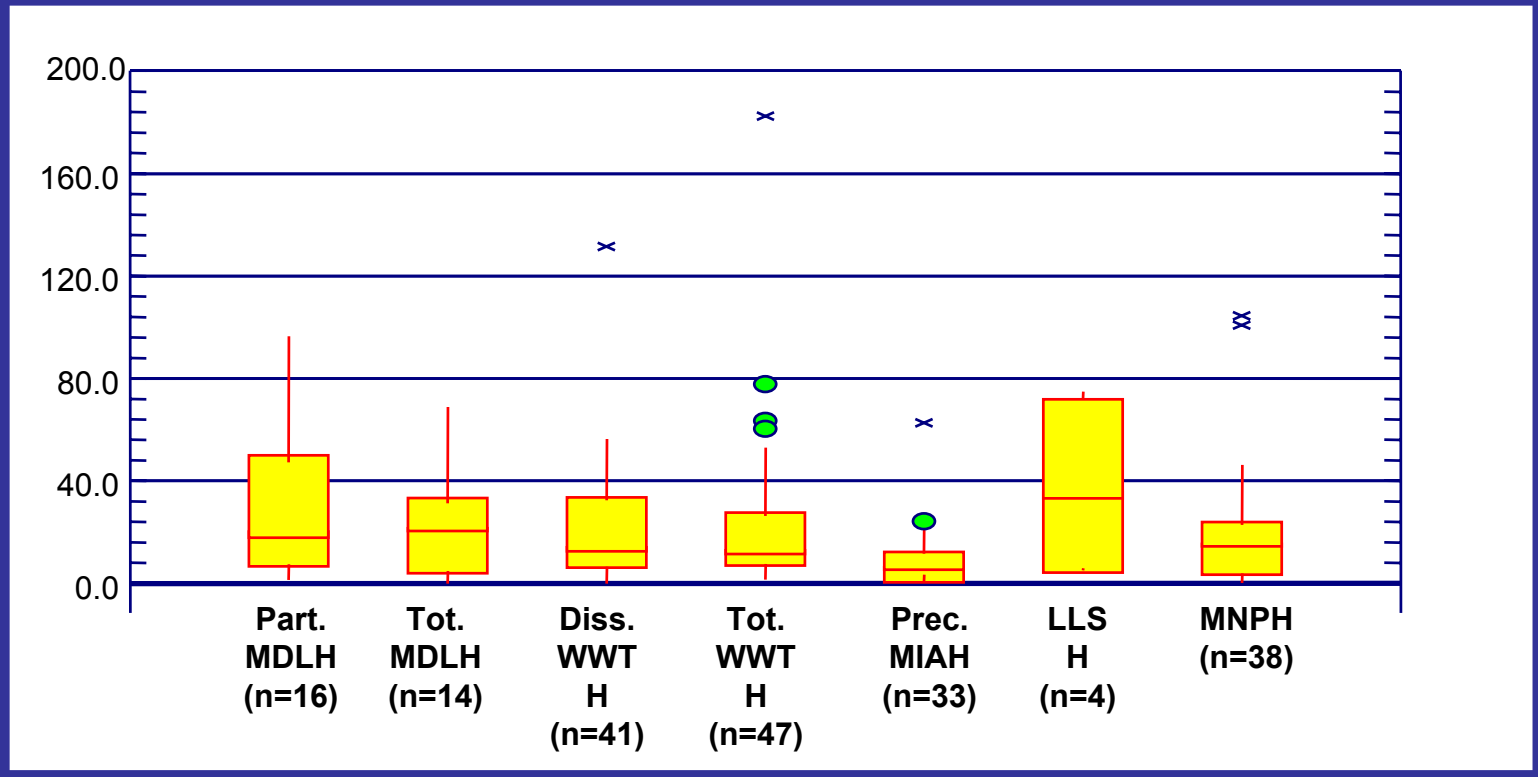
- Challenges
  - Comparison of various analysis detection limit measures (e.g., differences of MDL, SDL, DDL, etc.)
  - Detection limits not reported for some analytes (e.g., some nutrients)

Precision

- Assessed through Relative Percent Differences (RPDs) or Relative Standard Deviations (RSDs) where more than one duplicate analyzed.
- Examine distribution and summary statistics of RPD/RSDs.
- Stratify calculations where appropriate
  - Filter Fraction/Phase
  - Whether above or below detection limit

System Precision

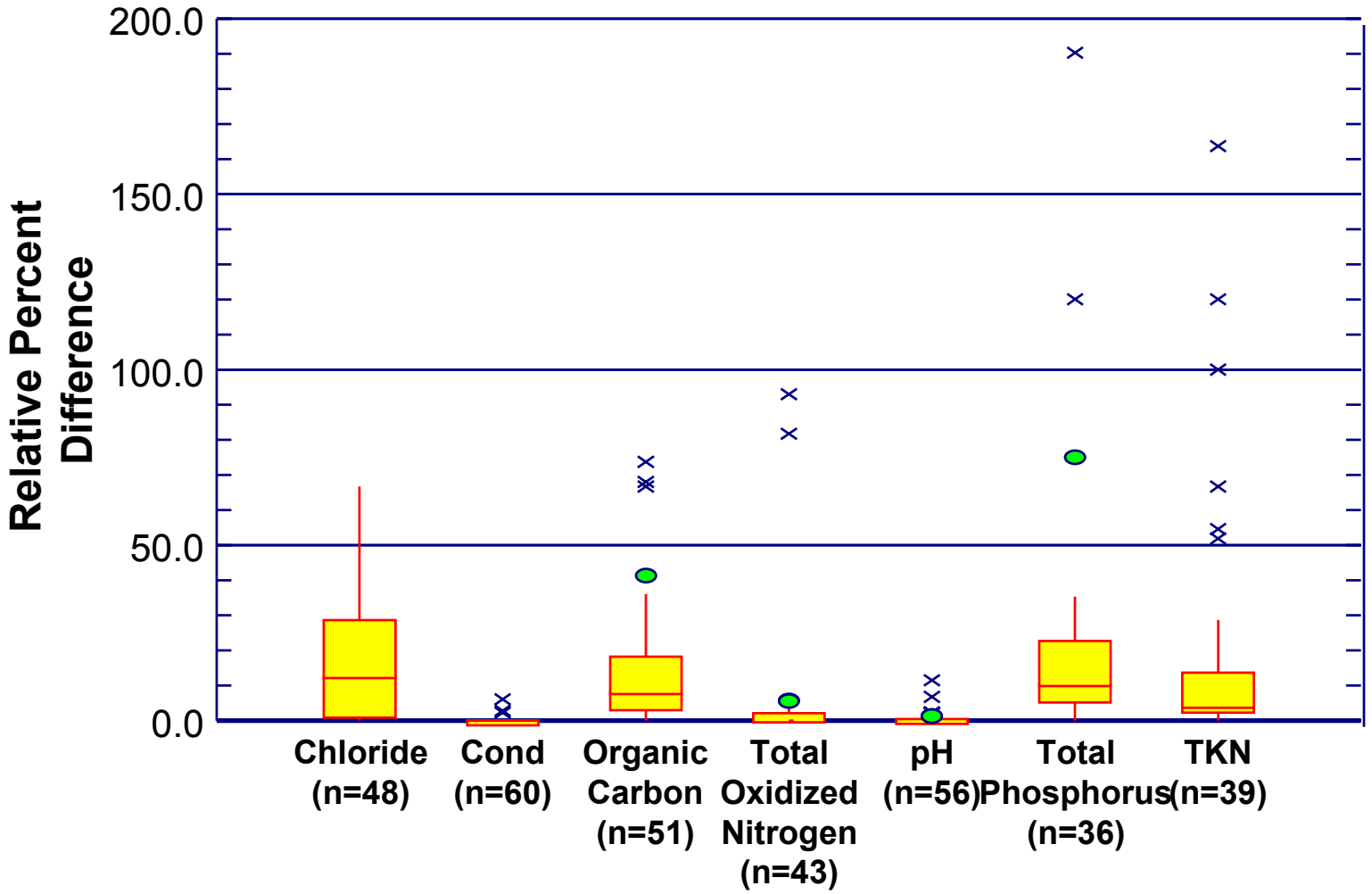
RPDs Between RFS and Field Duplicates Hg



- MIAH estimates biased low due to re-analysis of failed field duplicates and unreported results for failed field duplicates
- Field duplicates reported only for one MIAH phase

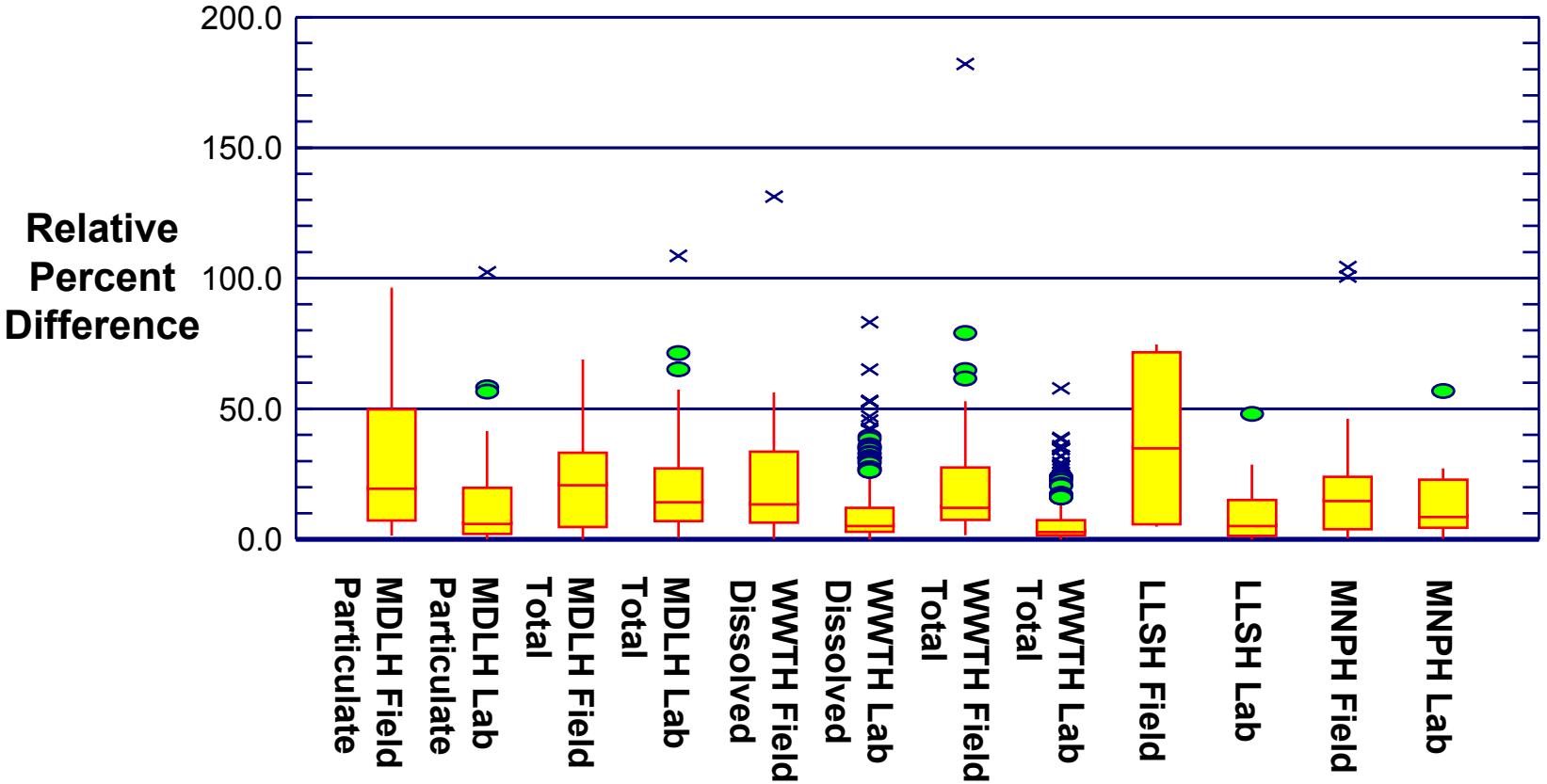
Analytical Precision

RPDs between RFS and Lab Duplicates GRAN



Precision

Comparison of RPDs for Field Duplicates and Lab Duplicates - Mercury Focuses



Precision

- Challenges
  - Some estimates may be biased:
    - RULA - questionable estimate because FDs statistically higher than matching RFS
    - MIAH - low biased because not all duplicate results that failed were reported
  - Additional field (FD2, FD3) and lab replicates (LD2-LD4) collected for some focuses. Comparison of RPDs and RSDs may not be appropriate.
  - Some focuses collected only sequential field duplicates (WWTH), or a combination of FDs and SFDs (USTN)

Precision

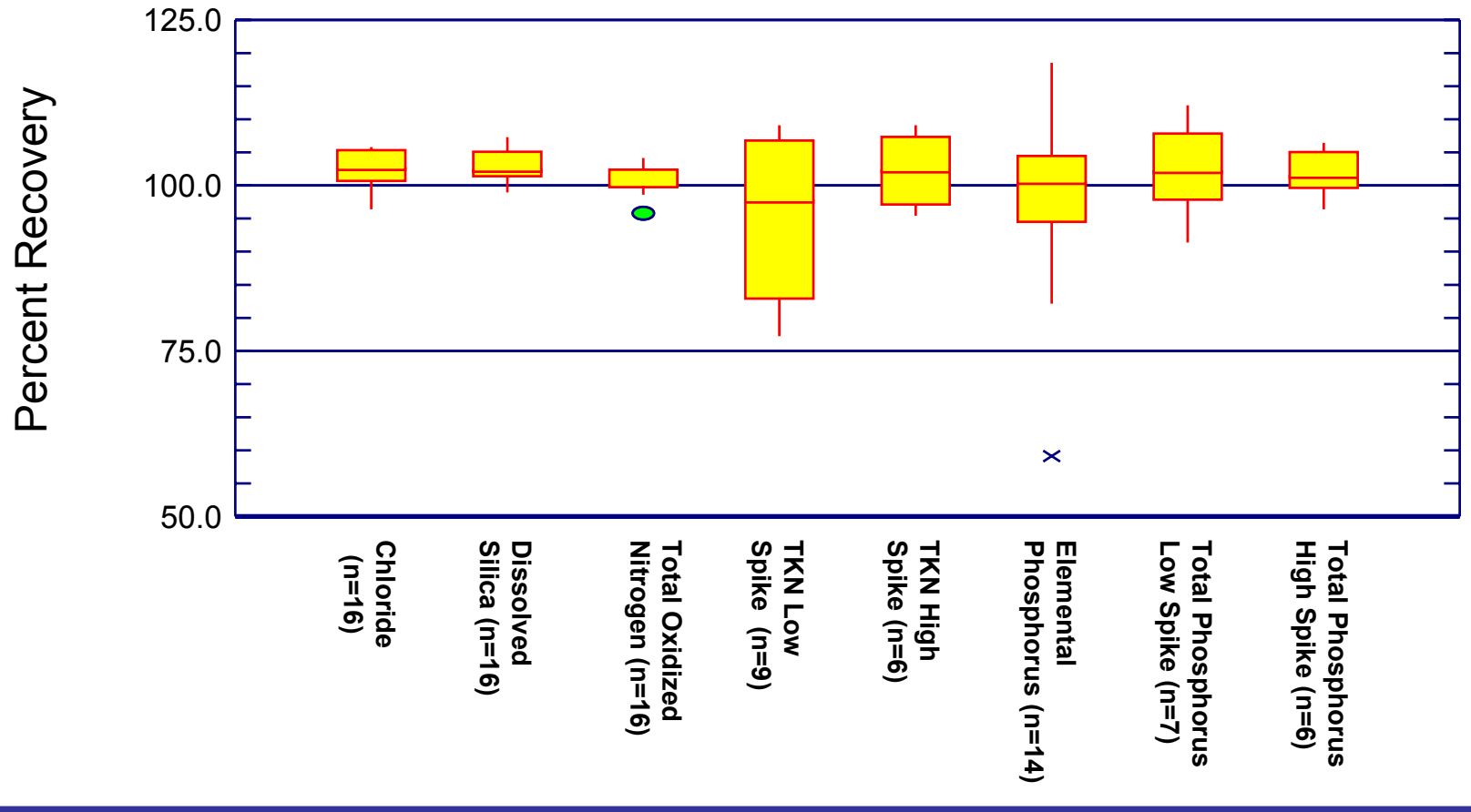
- Challenges (con't)
  - Number of duplicates varied widely (each sampling episode not always represented equally)

Bias

- Estimated using spiked samples
- Statistic of Interest: Percent Recovery
  - if mean > 100% some high bias, < 100% low bias
- System Bias: Field Control solutions
- Analytical Bias:
  - Lab Matrix Spikes, Lab Performance Checks, Standard Checks (high, low)

System Bias

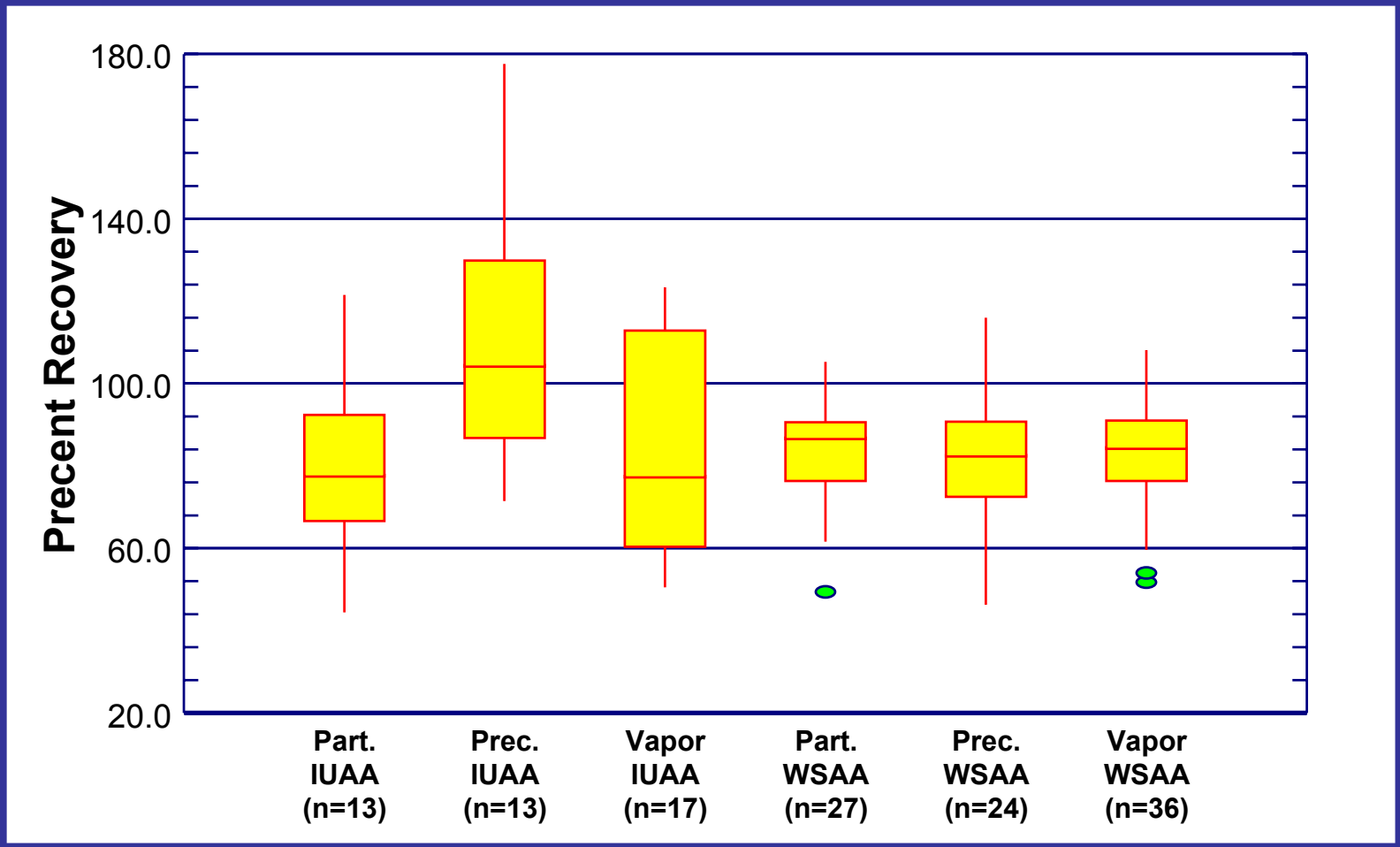
Percent Recovery of Field Control Solutions - FCM



- No FCM data for Orthophosphate or Ammonium Nitrogen

Analytical Bias

Percent Recovery of Lab Matrix Spikes - Air Atrazine



Bias

- Issues
  - Data for system bias estimates not available for most focuses
  - Use of surrogate correction factors to assess bias reflects analytical bias - but because data was surrogate corrected, the bias estimate does not reflect final data
  - Comparison of various QCIDs
    - Reagent water spikes (no matrix effects) vs. RFS spikes (matrix effects)

Percentage of Variability due to Sampling and Analytical Measurement Uncertainty

- Estimating two Components of Variation
  - Variation due to Sampling and Analytical Measurement Uncertainty (Component 1)
  - Total System Variation (Component 2)
- Percentage due to Sampling and Analytical Measurement Uncertainty is estimated as the ratio of the two components (Component 1/Component 2)
- Desirable for the components to be estimated using consistent methods for all focuses to allow for valid comparison among focuses

Percentage of Variability due to Sampling and Analytical Measurement Uncertainty

- Component 1 (Variance due to sampling and analytical measurement uncertainty)-Estimated using Bootstrap Estimation Procedure, based on ANOVA
  - allows ANOVA assumptions to be met
    - Normality
    - Constant pair variance
- Estimation based on Mean-Squared Error (MSE):

$$s^2_w = \text{MSE} = \frac{1}{n} \Sigma_{i \in (1,..,n)} s^2_{(RFS_i,\, FD_i)}$$

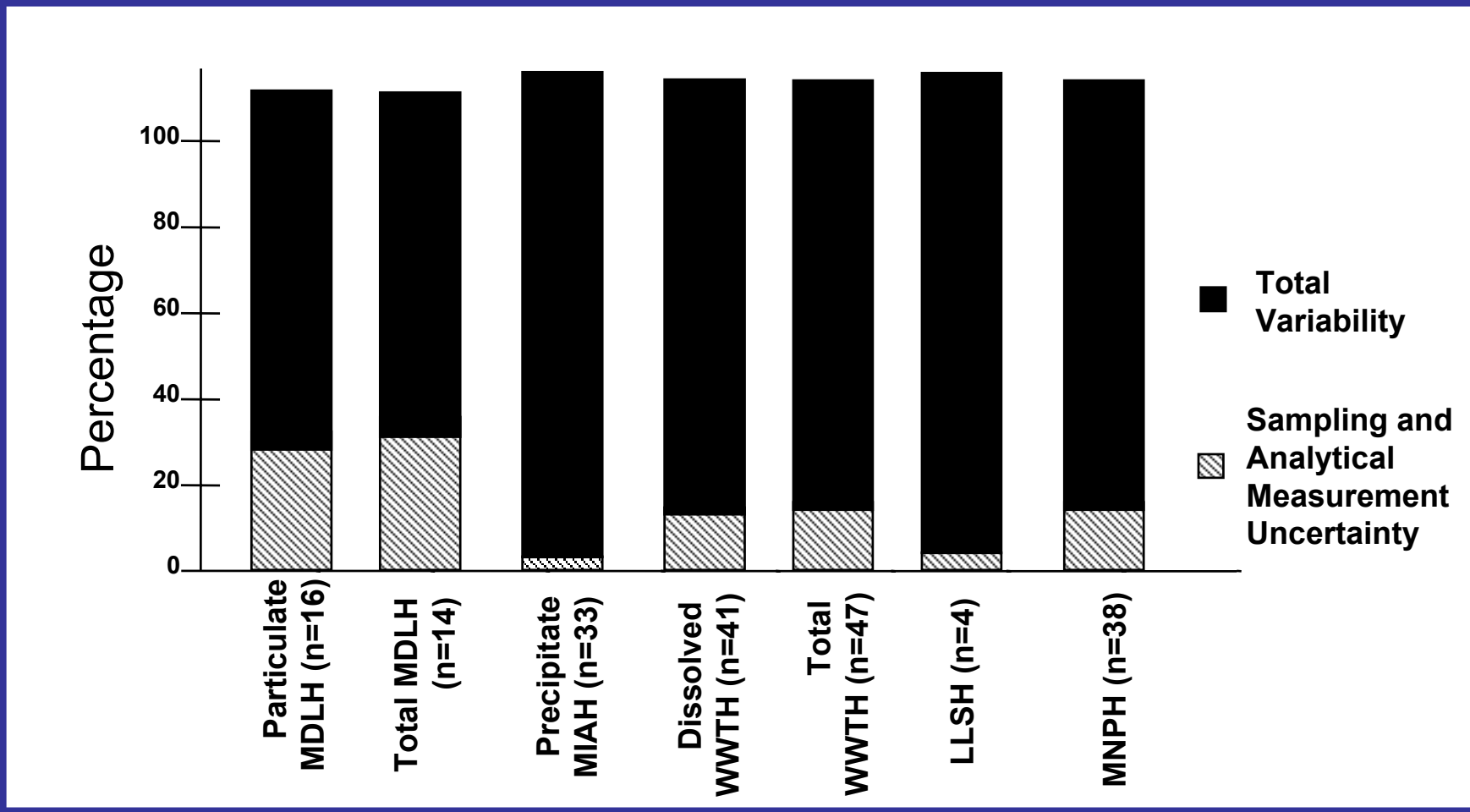
The MSE is calculated 5,000 times. For each repetition j (from 1 to 5,000), the MSE*j is calculated using a random selection of the original pair variances.

- The mean of the 5,000 estimated MSE*j values is an estimate of Component 1.

Percentage of Variability due to Sampling and Analytical Measurement Uncertainty

- Component 2 (total variability)- estimated using the variance of all RFS results
  - Assumption of Normality tested using D'Agostino or Shapiro-Wilk tests
  - If data are not normally distributed, results are log-transformed, and tested again. If the log-transformed data fit normality, Components 1 and 2 are calculated using log transformation.
  - If both untransformed and log-transformed data show large departures from normality, Bootstrap estimation procedure is used to estimate Component 2.
  - Because of the large number of RFS results in most focuses minor departures from normality or log-normality can be accepted

Percentage of Variability due to Sampling and Analytical Measurement Uncertainty



- MIAH estimate low biased due to unreported duplicates
- WWTH duplicates SFD1, not FD1

Percentage of Variability due to Sampling and Analytical Measurement Uncertainty

- Challenges
  - Estimate dependent on type and number of field duplicates
  - Calculated percentages may be misleading. A low percentage could be caused by good precision or large overall variability.